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Crystal and molecular structure of di-*tert*-butylhydridosilanol[☆]

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Abstract

The single-crystal X-ray structure analysis is reported of *t*-$Bu_2SiH(OH)$. In the crystal lattice, four molecules of the title compound are connected via hydrogen bridges showing an eight-membered O_4H_4 ring structural motif. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Silicon; Silanol; Hydrogen bonding; X-ray structure

1. Introduction

Organosilanols represent a well established class of compounds. So far, more than 100 organosilanols were subject of single-crystal X-ray diffraction studies [1]. All of these compounds realize intra- and/or intermolecular hydrogen bonds in the solid state with a fascinating variety of structural motifs. We are aware of only one example, namely 1,1,3,3,5,5,7,7-octaphenyltetrasiloxan-1,7-diol, showing no hydrogen bonding [1d]. The understanding of the directing forces which control the organization and assembly from single molecules to complex hydrogen bonded frameworks upon crystallization is rather limited [2]. In the context of crystal engineering such knowledge would be extremely helpful to design material properties on a molecular level. Therefore the collection of many structural data is welcome. Organosilanols find applications as building blocks for molecular metallasiloxanes [3]. In this area our interests are mainly focused on the chemistry of stannasiloxanes [4] and in this context we prepared the title compound *t*-$Bu_2SiH(OH)$ according to the method of Barton and Tully [5]. Some time ago the latter compound was applied for the preparation of the di-*tert*-butylsilanone radical anion [6]. Herein we describe the single-crystal X-ray structure of *t*-$Bu_2SiH(OH)$.

2. Experimental

The title compound was prepared according to the literature method [5] to give colorless crystals of m.p. 65–66°C, ^{29}Si-NMR ($CDCl_3$) δ 12.7 ppm. A single crystal of *t*-$Bu_2SiH(OH)$ suitable for X-ray analysis was taken from the wall of the vessel where the compound sublimed after several weeks at room temperature.

Crystal data and structure solution of *t*-$Bu_2SiH(OH)$: $C_8H_{20}OSi$, $M_r = 160.33$, tetragonal, I-4, $a = b = 15.681(1)$, $c = 9.080(1)$ Å, $V = 2232.7(3)$ Å^3, $Z = 8$, $D_x = 0.954$ g cm^{-3} $\lambda(\text{Mo–K}_\alpha) = 0.71069$ Å, $F(000) = 720$, $m = 0.160$ mm^{-1}, $T = 173(1)$ K. The data were collected to a maximum θ of 25.30° with 360 frames via ω-rotation ($\Delta/\omega = 1°$) at two times 5 s per frame on a Nonius Kappa CCD diffractometer with a completeness of 88.6% (95.7% with θ_{max} of 22.45°). The structure was solved by direct methods SHELXS-97 [7a] and refined by full-matrix least-squares calculations using all measured F^2 data and SHELXL-97 [7b]. All non-H atoms were refined anisotropically.

The Si(1)-bonded hydrogen atom H(2) was located in the difference Fourier map and refined isotropically. The other H atoms were placed in geometrically calculated positions using a riding model (including free rotation about C–C or Si–O, respectively) and refined with common isotropic temperature factors for differ-

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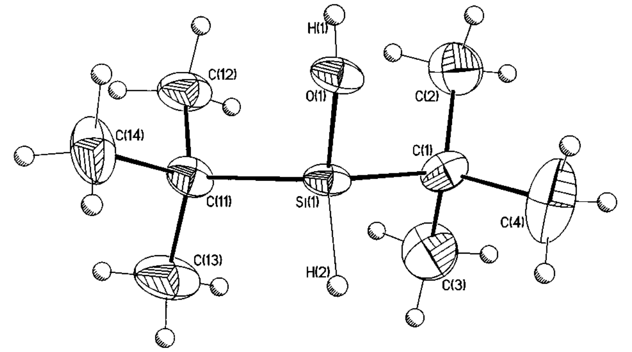

Fig. 1. General view (SHELXTL-PLUS) of a molecule of *t*-$Bu_2SiH(OH)$ showing 30% probability displacement ellipsoids and the atom numbering scheme.

ent H types (C–$H_{prim.}$ 0.96 Å, U_{iso} 0.125(7) $Å^2$; O–H 0.82 Å, U_{iso} 0.03(1) $Å^2$). A disordered *t*-Bu group was found with occupancies of 0.8 (C(14)) and 0.2 (C(14′)). The absolute configuration for *t*-$Bu_2SiH(OH)$ could not be determined by refinement of the Flack [7c] parameter 0.4(3). The correctness of the absolute configuration was deduced from the X-ray data by comparison of the *R* values of this and the inverted structure. $R_1 = 0.0639$ for 1447 $[I > 2\sigma(I)]$ and $wR_2 = 0.1611$ for 1816 independent reflections. The max. and min. residual electron densities were 0.594 and -0.364 e $Å^{-3}$. The molecular structure is shown in Fig. 1. Selected bond lengths and angles are listed in Table 1.

3. Discussion

The silicon atom shows a distorted tetrahedral configuration with the C–Si–C bond angle being 117.9(2)° as a result of the steric demand of the *tert*-butyl groups. In the closely related organosilanol derivative *t*-$Bu_2Si(F)OH$ this angle is 120.5(6)° [8a]. The Si–O bond length amounts to 1.651(3) Å which is longer than the corresponding Si–O distance of 1.613(7) Å in *t*-$Bu_2Si(F)OH$ [8a]. The Si–C distances of 1.882(5) and 1.880(5) Å are comparable with those of the related organofluorosilanol mentioned above [8a]. In the crystal lattice there are short intramolecular O···O distances of 2.701(4) Å which indicate hydrogen bridges. Thus, four molecules of *t*-$Bu_2SiH(OH)$ are connected with each other via hydrogen bridges realizing an eight-membered O_4H_4-ring (Fig. 2). The same structural motif is present in *t*-$Bu_2SiF(OH)$ (O···O distance 2.756(9) Å [8a], Ph_3SiOH (O···O distances between 2.637(5) and 2.684(6) Å) [8b], Ph_3GeOH (O···O distances between 2.609(11) and 2.657(11) Å) [8c] and in Ph_3COH (O···O distances between 2.80(3) and 2.90(3) Å) [8d]. Obviously, the different substituent patterns at silicon in the three organosilanols as well as the replacement of silicon by carbon and germanium, respectively, have only a small influence on the general structural motif, i.e. formation of tetramers.

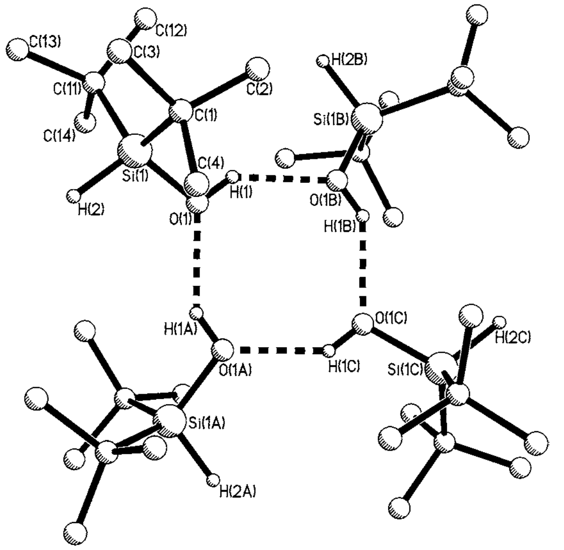

Fig. 2. View (SHELXTL-PLUS) of the hydrogen bonding in the crystal lattice of *t*-$Bu_2SiH(OH)$. Symmetry codes used to generate equivalent atoms: *a* = *y*, − *x*, − *z*; *b* = − *y*, *x*, *z*; *c* = − *x*, − *y*, *z*.

Table 1
Selected bond lengths (Å) and angles (°) for *t*-$Bu_2SiH(OH)$ [a]

Si(1)–O(1)	1.651(3)	Si(1)–C(1)	1.882(5)
Si(1)–C(11)	1.880(5)	Si(1)–H(2)	1.38(5)
O(1)–O(1a)	2.701(4)		
O(1)–Si(1)–C(1)	108.9(2)	O(1)–Si(1)–C(11)	109.5(2)
C(11)–Si(1)–C(1)	117.9(2)	O(1)–Si(1)–H(2)	110(2)
C(1)–Si(1)–H(2)	104(2)	C(11)–Si(1)–H(2)	106(2)
O(1)–H(1)–O(1a)	142.9	Si(1)–O(1)–H(1)	109.5

[a] Symmetry transformations used to generate equivalent atoms: *a* = *y*, − *x*, − *z*.

However, there seems to be an influence of these parameters on the planarity of the four oxygens in the tetramers. Thus, the oxygen atoms in *t*-$Bu_2Si(H)OH$ are planar to ± 0.022(3) Å with the silicon atoms being alternating displaced by 0.666(1) Å above and below this plane, respectively.

In *t*-$Bu_2Si(F)OH$ the deviation of the oxygens from the plane amounts to ± 0.2 Å whereas in the other tetramers mentioned above the four oxygens form flattened tetrahedrons [8a–d].

The tetramer of the title compound exhibits a propeller-type arrangement with the *t*-butyl groups pointing in clockwise direction, and hence it is chiral (Fig. 2).

The X-ray structures of *t*-$Bu_2Si(H)OH$ and of $(Ph_2MeSi)CMeSiH(OH)$ [9] are the only known examples for diorgano(hydrido)silanols so far.

4. Supplementary material

Crystallographic data for the analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 136797 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: + 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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